REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
27-05-2014	Final Report	1-Jul-2013 - 31-Mar-2014

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Inducing the Formation of Functional Macroscopic Assemblies Through Programmed Orthogonal Supramolecular Interactions	W911NF-13-1-0236
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
	611102

6. AUTHORS	5d. PROJECT NUMBER
Adam B. Braunschweig	
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES	8. PERFORMING ORGANIZATION REPORT NUMBER
University of Miami - Coral Gables 1320 South Dixie Hwy. Suite 650 LOC 2960 Coral Gables, FL 33146 -2926	

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211	ARO
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)
	64125-CH-II.3

12. DISTRIBUTION AVAILIBILITY STATEMENT

Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES

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14. ABSTRACT

A novel supramolecular system composed of diketopyrrolopyrrole electron donors and perylene derived bisimide (PDI) electron acceptors forms superstructures that undergo fast photoinduced charge separation following assembly. This bio-inspired route towards functional hierarchical structures, whereby assembly and electronic properties are closely coupled, could lead to new materials for artificial photosynthesis and organic electronics.

15. SUBJECT TERMS

Self-assembly, macromolecules, donor-acceptor

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE	UU		Adam Braunschweig
UU	UU	UU			19b. TELEPHONE NUMBER
					305-284-2516

Report Title

Inducing the Formation of Functional Macroscopic Assemblies Through Programmed Orthogonal Supramolecular Interactions

ABSTRACT

A novel supramolecular system composed of diketopyrrolopyrrole electron donors and perylene derived bisimide (PDI) electron acceptors forms superstructures that undergo fast photoinduced charge separation following assembly. This bio-inspired route towards functional hierarchical structures, whereby assembly and electronic properties are closely coupled, could lead to new materials for artificial photosynthesis and organic electronics.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
05/22/2014	1.00	David Ley, Carmen X Guzman, Karin H Adolfsson, Amy M. Scott, Adam B. Braunschweig. Cooperatively Assembling Donor-Acceptor Superstructures Direct Energy Into an Emergent Charge Separated State, Journal of the American Chemical Society, (05 2014): 0. doi: 10.1021/ja5015053
05/27/2014	2.00	Amy M. Scott, Adam B. Braunschweig, David Ley, Carmen X. Guzman, Karin H. Adolfsson. Cooperatively Assembling Donor–Acceptor Superstructures Direct Energy Into an Emergent Charge Separated State, Journal of the American Chemical Society, (05 2014): 0. doi: 10.1021/ja5015053
TOTAL:	**2**	

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received	Paper
TOTAL:	

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Fusion Functional Polymeric Materials, Cancun, Mexico, 12 February 2014
"Emergent Charge Transfer in Cooperatively Assembling Donor-Acceptor Superstructures"

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received   Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received   Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received   Paper

TOTAL:

Number of Manuscripts:

Books

Received   Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

American Chemical Society, Division of Polymeric Materials: Science and Engineering (PMSE) Young Investigator Award 2014

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Carmen X. Guzman	0.00	
FTE Equivalent:	**0.00**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
David Ley	0.89
FTE Equivalent:	**0.89**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Adam Braunschweig	0.30	
FTE Equivalent:	**0.30**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics
This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME   PERCENT_SUPPORTED

**FTE Equivalent:**
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

see attachment.

Technology Transfer

FINAL REPORT W911NF-12-1-0125. Donor-Acceptor Superstructures With Emergent Stimuli Responses for Molecular Information Processing. PI. Adam B. Braunschweig, University of Miami, Coral Gables, FL 33146. Email: a.braunschweig@miami.edu

1. Statement of the Problem Studied. The goal of the proposed work was the design and synthesis of a supramolecular system possessing two broadly absorbing, redox active molecules with appropriately matched HOMO and LUMO energy levels. Electron donors based on diketopyrrolopyrrole (DPP), and electron acceptors based on the perylene derived bisimide (PDI) scaffolds were chosen because of their easy preparation and their synthetic modularity. Self-organization *via* noncovalent supramolecular interactions brings the donor and acceptor molecules into close proximity, so that photoexcitation would result in efficient charge separation, while conductive channels through the π-stacking columns of the system would facilitate further charge separation. While numerous covalently bound donor-acceptor devices are already known, this supramolecular approach towards self-organization and emergent properties was pursued to reduce synthetic efforts while maximizing structural complexity and enabling emergent properties. The primary aims of the proposed work were (1) to develop a system that assembles into complex superstructures and undergoes aggregation driven photoinduced charge separation, and (2) model biological systems where complex properties emerge following supramolecular assembly.
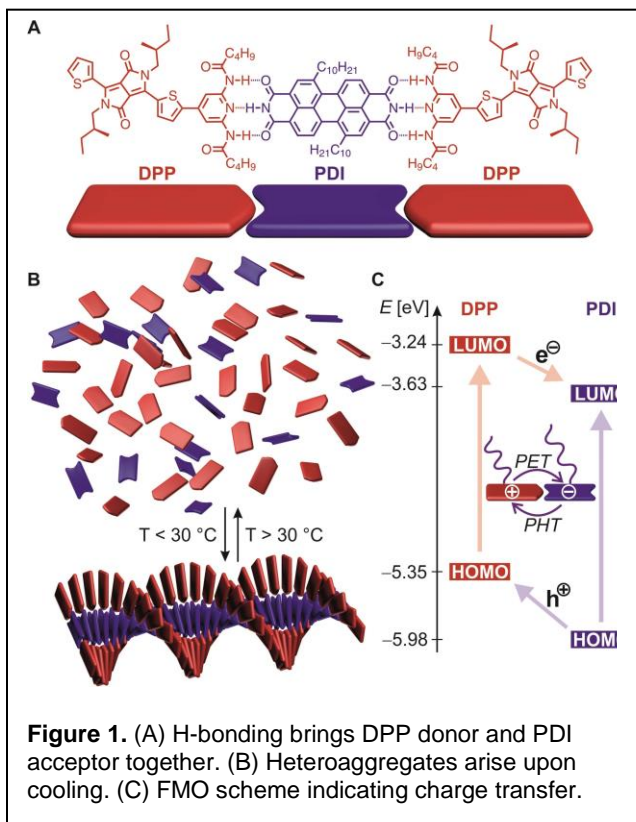
Figure 1. (A) H-bonding brings DPP donor and PDI acceptor together. (B) Heteroaggregates arise upon cooling. (C) FMO scheme indicating charge transfer.
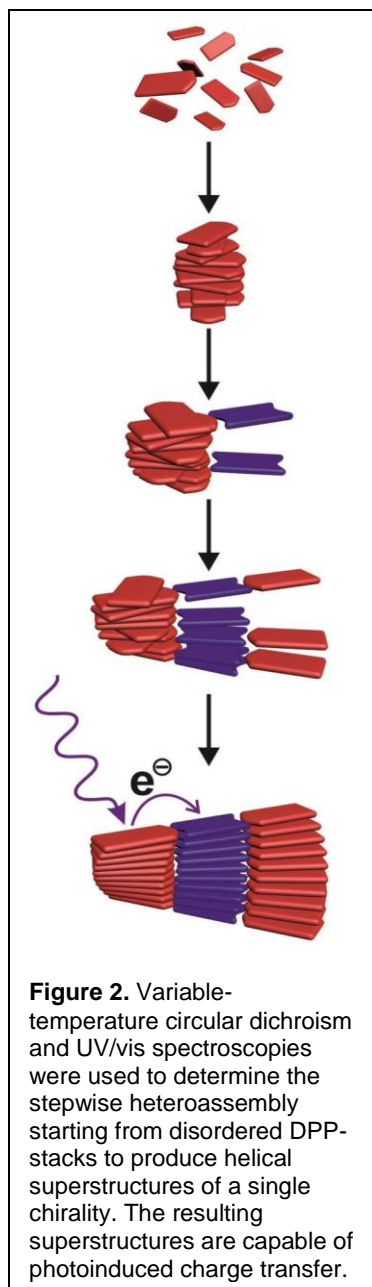
2. Summary of Most Important Results. The modular synthesis of chiral and achiral DPP donors and 1,7-substituted PDI acceptors,[1] their assembly into ordered superstructures, and finally the ultrafast dynamics of these systems following photoexcitation were already described. Previously, we have shown that the DPP-PDI donor-acceptor system undergoes thermodynamically driven self-organization *via* multiple noncovalent interactions, bringing the complementary redox active parts into close proximity, which results in an ability to form a charge separated state following light absorption.

Substituted DPP donors and PDI acceptors are prepared efficiently *via* organic synthesis consisting of only a few steps,[2,3] and the band gaps and

absorption maxima can be tuned by varying the substituents.[4] Orthogonal noncovalent interactions were programmed into these compounds to drive the supramolecular assembly of DPP and PDI. We found that the heteroaggregation process occurs following a recently described cooperative assembly path (Figure 2): driven by the strongest interaction in the system, the DPP units first form disordered homoaggregates[5] *via* π-stacking, while in the next step, PDI units are associated to the DPP stacks by means of triple H-bonding.[1] This binding model allows the preparation of heteroaggregates with a varying ratio of DPP to PDI.

Having demonstrated the complementary binding mechanism that results in the thermodynamically driven formation of ordered heteroaggregates, we proceeded to investigate the optoelectronic properties of the system and to assess the ability to undergo photoinduced charge separation and subsequent charge separation to create a long-lived radical pair state, which is a prerequisite for efficient light harvesting. The ground state frontier molecular orbital (FMO) energy levels of the individual compounds were investigated by cyclic voltammetry (CV), UV/vis and fluorescence spectroscopy, to study whether the system can undergo thermodynamically favored charge separation upon photoexcitation. Our studies revealed that the energetic positions of the FMOs do allow the reduction of the PDI acceptor by the photoexcited DPP donor (electron transfer), or the oxidation of the DPP donor by the photoexcited PDI acceptor (hole transfer). Based on the FMOs of the individual compounds, electron transfer can occur by the transfer of an electron from the upper SOMO (–3.24 eV) of photoexcited DPP into the LUMO (–3.63 eV) of PDI, while the hole transfer route corresponds to the transfer of an electron from the DPP HOMO (–5.98 eV) into the lower SOMO (–5.35 eV) of photoexcited PDI. The driving forces are –0.39 eV for electron transfer from DPP to PDI, and –0.63 eV for hole transfer from PDI to DPP (Figure 1C).[6]

To take reorganization energies of the ionic species and solvent effects in account, the charge separation energies (ΔG_{CS}) were calculated by performing the Weller correction[7] on the measured reduction and oxidation potentials. With respect to the ground state, the charge separation energy was 2.0 eV (620 nm),[6] which corresponds to the absorption band in the visible spectrum that the aggregate exhibits.[1] This is a new absorption band, which is not present in the individual components, and vanishes

Figure 2. Variable-temperature circular dichroism and UV/vis spectroscopies were used to determine the stepwise heteroassembly starting from disordered DPP-stacks to produce helical superstructures of a single chirality. The resulting superstructures are capable of photoinduced charge transfer.

upon thermally or chemically induced disaggregation of the supramolecular aggregates. This indicates that the direct excitation of the system into its charge separate state is an emergent property of this donor-acceptor system that comes along with the formation of heterosuperstructures. To investigate the charge separation and recombination dynamics in detail, static reorganization energies λ_S were calculated by invoking the Marcus relation,[8-11] which is based on the dielectric continuum model of the solvent. As expected for toluene as a low polarity solvent, this static contribution ($\lambda_S = 0.03$ eV) is insignificantly small, so that the overall reorganization energy λ is given by the intrinsic value ($\lambda_i = 0.30$ eV), which was determined with density functional theory (DFT) computations using the ORCA program package.[12] The charge separation energy of a DPP-PDI assembly is –0.35 eV based on photoexcited PDI, so that the condition – $\Delta G = \lambda$ is fulfilled; so based on the Marcus equation, very fast electron transfer is expected to proceed from photoexcited PDI. As a result of the much larger free enthalpy for charge recombination ($\Delta G_{CR} = -2.00$ eV) that shifts this process into the Marcus inverted regime,[11] so recombination is expected to occur much slower than charge separation so that continuous excitation with visible light would efficiently result in a charge-separated steady-state. This donor-acceptor system therefore exemplifies how supramolecular assembly and FMO tailoring can be combined to achieve emergent charge transfer in hierarchical organic superstructures.
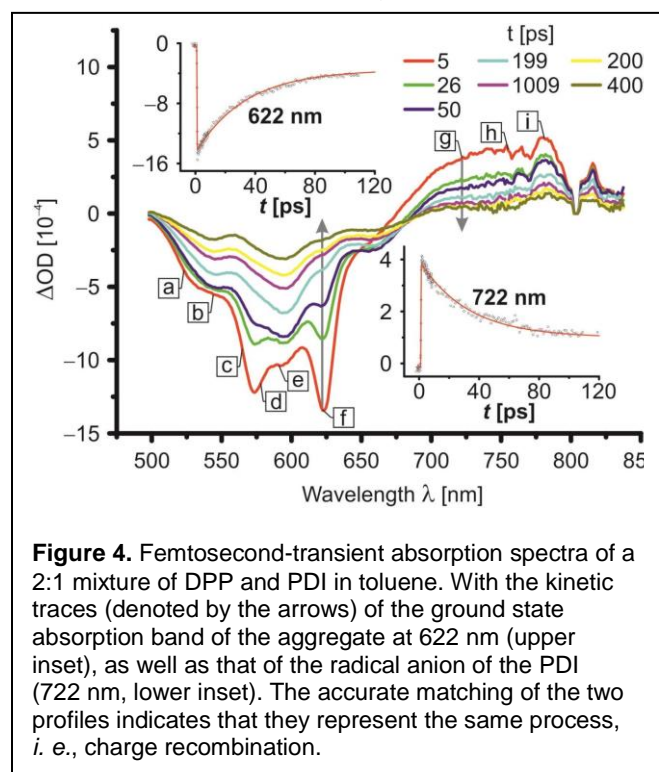
The ability of this system to undergo aggregation driven photoinduced charge separation was investigated by variable temperature (VT) fluorescence titrations. A 2:1 mixture of DPP (45 µM) and PDI (23 µM) in toluene was prepared and the fluorescence spectra were measured at twelve temperatures from 70 °C to 20 °C. The sample was photoexcited at 356 nm, where the DPP absorbance is three times greater than that of the PDI, providing for quasiselective photoexcitation of the donor. As controls, the individual components alone, as well as the stoichiometric mixture of DPP with an *N,N'*-dicyclohexyl protected PDI,

Figure 3. (A) VT fluorescence spectra of a 2:1 DPP:PDI mixture (45 µM, and 23 µM, respectively) in toluene ($\lambda_{Ex} = 356$ nm). (B) Fluorescence titration at 30 °C ($\lambda_{Ex} = 483$ nm), DPP equivalents given based on PDI. (C) Relative DPP fluorescence intensity at various temperatures. (D) Fluorescence quenching of PDI with increasing DPP concentration at various temperatures.

which is unable to H-bond with DPP, were measured under identical conditions.[6] The VT fluorescence study indicates that aggregation of the redox active donor and acceptor drives the photoinduced charge separation, which manifests as fluorescence quenching

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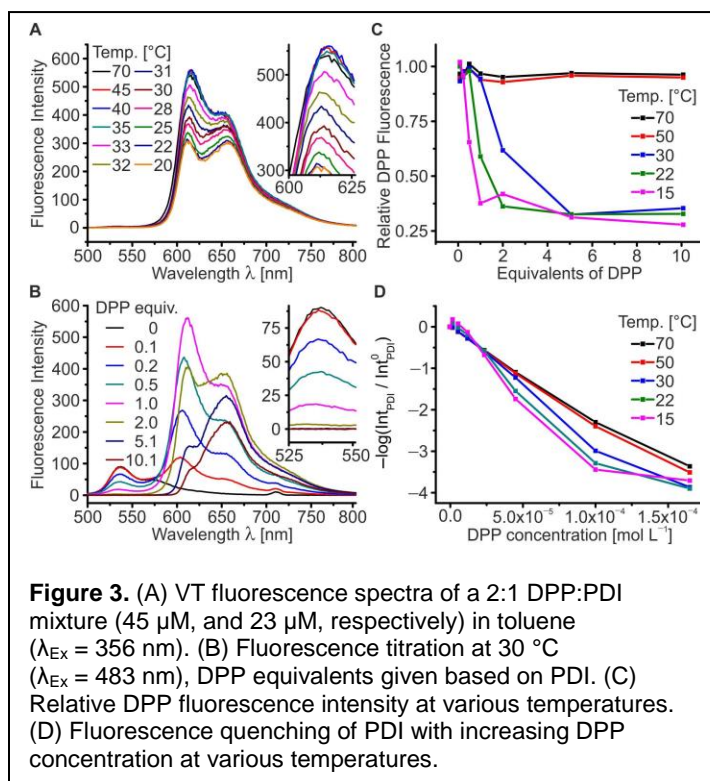
(Figure 3A): as the thermally disaggregated sample (70 °C) is slowly cooled down, the DPP intensity initially increases slightly. This reflects the classic notion that nonradiative decay of an excited state is typically promoted at higher temperatures (dynamic quenching). The DPP fluorescence intensity reaches a maximum at 40 °C, before it rapidly decreases in intensity with decreasing temperatures, and finally stabilizes at 20 °C. There is no measurable decrease in DPP fluorescence in absence of the PDI, or if the *N*,*N'*-dicyclohexyl protected PDI, which is incapable of Hydrogen bonding, is used, indicating that the association of PDI units with the DPP stacks is a prerequisite for photoinduced charge transfer.

The synergistic effects of concentration and temperature on the aggregation induced fluorescence was studied by a fluorescence quenching titration at variable temperatures (Figure 3B): to a solution of PDI in toluene (25 µM) was added a solution of DPP in toluene (481 µM), and the fluorescence spectra of the mixture were measured at 356 nm, and 483 nm, allowing quasi-selective photoexcitation of DPP and PDI, respectively. The resulting spectra were compared to those of the individual components, so that spectral changes occurring as a result of aggregation could be unambiguously assigned. The results of this titration show that at temperatures below 30 °C, and with increasing DPP concentration the fluorescence of the PDI is efficiently quenched (Figure 3C).[6] While at first glance it may seem unreasonable that the PDI can quench the fluorescence of more DPP units than it can bind *via* H-bonding, this behavior is in fact a subtle consequence of the cooperative heteroaggregation of this hierarchical system. The DPP first forms aggregates, followed by binding of PDI to the DPP stacks (Figure 2). The experimental observation that PDI quenches more DPP than it binds *via* H-bonding is indicative of the formation of donor-acceptor superstructures with a DPP:PDI ratio greater than 2:1, where excess DPP units can act as antenna molecules that transfer excitation energy towards the next DPP-PDI binding pair where then charge separation subsequently occurs.

Figure 4. Femtosecond-transient absorption spectra of a 2:1 mixture of DPP and PDI in toluene. With the kinetic traces (denoted by the arrows) of the ground state absorption band of the aggregate at 622 nm (upper inset), as well as that of the radical anion of the PDI (722 nm, lower inset). The accurate matching of the two profiles indicates that they represent the same process, *i. e.*, charge recombination.

Further experimental evidence for photoinduced charge transfer within these donor-acceptor superstructures was obtained by performing femtosecond transient absorption (fs-TA) spectroscopy at room temperature in toluene with the individual compounds, and with the 2:1 mixture (Figure 4).[6] Photoexcitation of DPP (83 µM) at 485 nm with ~150 fs laser pulses results in the appearance of ground state bleaching at 544 nm and 594 nm, where the ground state recovers monoexponentially with a time constant around 5 ns, which is near the time resolution of our detection system and agrees with fluorescence lifetimes of comparable structures. Positive transient features in the range of 700 to 800 nm decay with longer time, which indicates that the S_1 state of DPP undergoes inefficient singlet triplet crossing with a time constant that is approximately two times larger than the fluorescence lifetime. The fs-TA spectrum of the PDI shows a ground state bleaching feature at 523 nm, which is slightly red-shifted compared to the ground state absorption as a result of convolution with stimulated emission (536 nm), while a negative feature at 578 nm results from stimulated emission alone. The fs-TA spectra of the aggregates are clearly different from those of the individual compounds, as they express very strong ground state bleaches at 622 nm, which is a spectral signature of the aggregate and corresponds to photoexcitation of the system directly into its charge-separated state (Figure 4). This feature displays a rise that was buried in the 200 fs instrument response time of our detection system. The ground state corresponding to the negative feature at 622 nm recovers mainly monoexponentially (~71 %) with a time constant of 33 ± 0.5 ps, and importantly, this recovery is accompanied by the decay of a positive transient feature at 722 nm (33 ± 0.5 ps, ~70 %). The PDI radical anion was generated in solution to determine its spectral fingerprint by applying the fluoride reduction method,[13] and a broad peak appeared in the visible range as a broad peak around 720 nm. With the two time constants – charge separation bleaching and ground state recover – matching each other perfectly, and the positive feature matching the spectral range of the PDI radical anion, we assigned

Figure 5. Energy diagram of a DPP-PDI assembly in toluene. The lowest excited state of DPP (2.07 eV) is not shown, as it is almost isoenergetic with the charge transfer state, which is the lowest excited state of the system.

the observed ultrafast process as charge recombination between the PDI radical anion and the DPP radical cation. Even though we were able to generate the latter one electrochemically and characterize it *in situ*, we found no evidence for this species in our fs-TA spectra.[6] However, this is not surprising because radical cations are generally known to possess absorptions that are much broader and weaker than those of their radical anion counterparts.[14-16] In accordance with our results from applying the Weller

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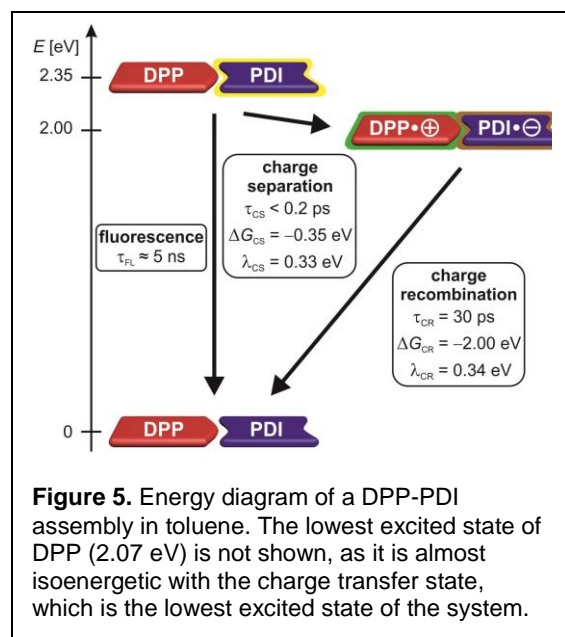
equation and the Marcus relation, the charge separated state constitutes the lowest excited state of this novel donor-acceptor assembly (Figure 5), and its formation is kinetically favored as the respective electron transfer occurs closely between the Marcus normal and inverted region and is therefore very fast. As charge recombination ($\tau_{CR} = 30$ ps) is much faster than fluorescence ($\tau_{FL} = 5$ ps), the photoexcited system mainly relaxes *via* the charge-separated state, explaining our experimental observation that the charge-separated state decays radiationless.[6]

In conclusion, we have designed and characterized a supramolecular system comprised of redox active, broadly absorbing DPP donors and PDI acceptors that are accessible *via* short and modular syntheses. The individual compounds are equipped with distinctive noncovalent binding sites, which drive thermodynamically favored assembly of the system into large, highly ordered heteroaggregates. Employing this self-assembly approach, complex hierarchical structures that are otherwise unattainable by classic covalent synthesis were prepared by harnessing the error-correcting nature thermodynamically driven supramolecular equilibrium. Importantly, the DPP-PDI supramolecular polymers investigated in the context of this proposal were a very important proof-of-concept demonstration that emergent properties could be designed following a biomimetic approach: a strategy that could be used to design sensors, energy harvesting devices, and electronic components for emerging military needs.

The results of the studies described above are disseminated in detail in a recently published manuscript: Ley, D.; Guzman, C. X.; Adolffson, K. H.; Scott, A. M.; Braunschweig, A. B.* "Emergent Charge Transfer in Cooperatively Assembling Donor-Acceptor Superstructures" *Journal of the American Chemical Society*, **2014**, *In Press*, DOI: 10.1021/ja5015053

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